JOURNAL OF CATALYSIS **102,** 116–125 (1986)

Hydrogenation of Olefin Adsorbed on Pt/SiO$_2$

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Received February 27, 1986; revised June 10, 1986

Cyclopentene and cyclooctene have been hydrogenated in a batch reactor on supported platinum catalysts at temperatures such that over 99.99% of the olefin was in the adsorbed state and primarily on the support. Reaction temperatures were −75°C for cyclopentene and −22°C for cyclooctene and $P(H_2)$ was usually 100 Torr. At coverages of one molecule of cyclopentene per nm^2 on Pt/(wide pore silica gel), the rate was zero order in olefin up to a conversion of about 70% following which the rate declined. The rate was about one-half order in hydrogen. Pt/alumina (PHF, American Cyanamid) and Pt/silica gel gave similar results. Transport of olefin from the surface of the support to crystallites of platinum occurred primarily by surface migration rather than through the vapor phase. Significant contribution to hydrogenation by hydrogen spillover from platinum to silica can be excluded. Small particles of platinum on silica gel gave somewhat larger values of turnover frequency, N_t, than did larger particles, at least after the pretreatment O$_2$,300°;H$_2$,300°;He,450°; cool in He. N_t for cyclopentene was roughly equal to that for propylene in conventional vapor phase hydrogenation extrapolated to −75°C. © 1986 Academic Press, Inc.

INTRODUCTION

In the usual gas-phase heterogeneous catalytic hydrogenation on a supported metal catalyst, the hydrogen and the olefin are in the gas phase. Hydrogen and olefin must undergo transport from the gas phase to the metal particles. Some olefin will detour via first adsorbing on the support and then migrating on the surface of the support to the metal. If the overall hydrogenation is zero order in olefin and if diffusional influences are small, this channel will not affect the overall rate, since direct vapor phase transport of olefin to the metal surface will be fast enough to keep the metal particles saturated with olefin (*1*). Suppose, however, that all of the olefin was adsorbed on the catalyst and primarily on the surface of the support. Hydrogen transport would be the same, but olefin transport would involve the motion of only ~30 nm from support to metal rather than motion of ~1 mm from the gas phase to inside the catalyst granule.

A report from this laboratory described the hydrogenation at −70°C of the stable free radical, di-t-butyl nitroxide, adsorbed on Pt/SiO$_2$ and Pt/Al$_2$O$_3$ (*2*). The rate was first order in the areal (surface) concentration of nitroxide.

$$(\text{t-bu})_2\text{NO}\cdot + \tfrac{1}{2}\text{H}_2 \rightarrow (\text{t-bu})_2\text{NOH}$$

This hydrogenation involves the addition of only one hydrogen atom to the nitroxide to form the hydroxylamine. At the beginning of the hydrogenation about 99% of the nitroxide was adsorbed on the surface of the support and a negligible amount was in the gas phase. One could imagine four transport procedures.

(a) Nitroxide molecules migrate over the surface of the silica gel to the surface of the platinum and react there with hydrogen atoms.

(b) Nitroxide molecules migrate to the platinum via the gas phase.

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0021-9517/86 $3.00

(c) The nitroxide is immobile, but the platinum particles migrate about the surface and hydrogenate the nitroxide molecules upon encounter.

(d) There is "spillover" of hydrogen atoms from the platinum to the support. Hydrogen atoms in some unknown form migrate over the surface of the support and react upon encounter with the nitroxide molecules.

The data appeared best to accord with procedure (a).

The present paper reports the more conventional hydrogenation of olefins adsorbed on supported platinum catalysts, primarily cyclopentene on Pt/SiO$_2$ catalysts at −75°C. In the previous work, the course of hydrogenation had been followed by measurement of the EPR signal of the nitroxide. In the present work, conversion vs time was followed by measurement of the consumption of hydrogen.

In addition to the hydrogenation of adsorbed nitroxide (*2*), other hydrogenations of adsorbed unsaturated molecules on supported metal catalysts have been reported. Miyata *et al.* described the hydrogenation of acetone adsorbed on 15 wt% Ni/SiO$_2$ at 25°C as followed by IR spectroscopy (*3*). The reaction was reversible, since upon warming to 50°C, 80% of the previously consumed hydrogen was evolved but negligible acetone or isopropyl alcohol. Primet *et al.* measured spectroscopically the rate of hydrogenation at 40°C of benzene on Y zeolite with low loadings of platinum (*4*). The rate of hydrogenation was first order in P(H$_2$) and zero order in the areal concentration of benzene. Since the pressure of hydrogen was constant during a run and the rate of hydrogenation was independent of time, they concluded that hydrogen spillover was not involved. Had spillover been involved, they assumed that the rate would be that of the surface reaction between spilled-over hydrogen and benzene. Thus, the rate at constant pressure of hydrogen would have decreased with time, whereas, in fact, it was independent of time.

EXPERIMENTAL

Materials. Cyclopentene (Chemical Samples Co., 99.9%) was refluxed over potassium and distilled under nitrogen into a storage bulb attached to the apparatus. It was then degassed by repeated freeze–thaw cycles. Cyclooctene (Chemical Samples Co., 99%) was treated similarly. Hydrogen was prepared in an electrolytic generator (Elhygen of the Milton Roy Co.) in which the hydrogen generated passes through palladium–silver alloy. Just before the reactor, hydrogen and helium passed through a silica gel trap cooled with liquid nitrogen and then a trap of Mn^{2+}/SiO$_2$. The latter trap reduces the content in oxygen to 1 ppb (*5*). Oxygen entered the apparatus through a trap of silica gel cooled with dry ice.

63.5-Pt/SiO$_2$-IonX-L (0.49 wt% Pt, prepared by ion exchange of 70–80 mesh Davison grade 62 silica gel with Pt(NH$_3$)$_4^{2+}$) and 27-Pt/SiO$_2$-IonX-S (1.48 wt% Pt on 120–140 mesh gel) have been described (*6*). The initial number is the percentage exposed measured by hydrogen chemisorption. 91.7-Pt/SiO$_2$-IonX-S (2.64 wt% Pt on 120–140 mesh gel) was prepared in the same fashion by Dr. Y. Inoue.

47.2-Pt/SiO$_2$-S (4.94 wt% Pt) and 28.1-Pt/SiO$_2$-S (9.97 wt% Pt), both on 120–140 mesh silica gel, were prepared by ion exchange, dried in air at 90°C, exposed to the following sequence of flowing gases, H$_2$,300°,2; O$_2$,300°,2;H$_2$,300°,2, and cooled to room temperature in flowing hydrogen. Here, H$_2$, 300°,2 indicates treatment in flowing hydrogen at 300°C for 2 h. A short He purge separated treatments by hydrogen and oxygen. The grade 62 silica gel had a specific area of 265 m^2 g^{-1}, a specific pore volume of 1.1 cm^3, and an average pore diameter of 14 nm. 40-Pt-Al$_2$O$_3$, prepared by Dr. M. Kobayashi, had served as a higher loading Pt/Al$_2$O$_3$ for examination by X-ray diffraction (*7*). It was prepared by impregnating American Cyanamid PHF alumina with an aqueous solution of Pt(NH$_3$)$_4$(NO$_3$)$_2$ to a plati-

TABLE 1

Catalysts

Catalyst	Pt_s (μmol g^{-1})	Pt particles[a] ($g^{-1} \times 10^{-16}$)	d[b]	N_t[c]	% as zero order[d]
91.7-Pt/SiO_2	124	127	0.12	0.010	70
63.5-Pt/SiO_2	16	7.8	0.48	0.0088	61
47.2-Pt/SiO_2	120	32	0.24	0.0075	70
28.1-Pt/SiO_2	143	13.8	0.36	0.0025	62
27-Pt/SiO_2	21	1.8	(1.0)	0.0035	39
40-Pt/Al_2O_3	72(116)	14(22)	0.28		

[a] Number of particles of Pt per g of catalyst assuming that the particles are spherical.

[b] Average distance between the particles of Pt relative to 27-Pt/SiO_2, for which $d \approx 120$ nm.

[c] Turnover frequency per sec^{-1} per Pt_s at −75°C, $P(H_2) = 100$ Torr, 1 molecule of cyclopentene per nm^2, standard pretreatment, taken from the zero order section.

[d] The percentage of the course of hydrogenation proceeding as zero order.

num loading of 3.5%. PHF alumina is a high purity γ-alumina (99.99%) with $a_s = 165$ m^2 g^{-1}. If one corrects to the same surface area as that of the silica, the values of moles of Pt_s and the number of Pt particles are those shown in parentheses in Table 1. The value for the average distance between particles in Table 1 was calculated assuming the texture of the alumina to be identical to that of the silica. However, the value should not be far from correct.

Experimental procedures. The apparatus is shown schematically in Fig. 1. All valves were Teflon needle valves. The amount of cyclopentene adsorbed on the catalyst was determined by measuring the pressure of cyclopentene in a dosing volume of known size followed by adsorption of the cyclopentene on the catalyst. The rate of hydrogen consumption was measured by the rate of decrease of the pressure of hydrogen in a known volume as read from a Barocel differential capacitance manometer connected to a recorder. At a maximum, when the pressure of hydrogen was 100 Torr, $\Delta P(H_2)$ at complete conversion was less than 7% of the initial pressure of the hydrogen. Thus, the system operated at constant volume and nearly at constant pressure.

The reactor was joined to the apparatus by Swagelock unions with Teflon ferrules. The catalyst (~1.0 g unless otherwise stated) was placed on the fritted glass disk in the reactor. The reactor area was evacuated and then filled with He at 25°C. The catalyst was then subjected to one of the following pretreatments. In the "standard" pretreatment, the catalyst was treated with flowing gases at about 60 cm^3 per min: O_2, 300°,0.5, the reactor area was evacuated, filled with helium, evacuated and this cycle repeated twice. The catalyst was then exposed to He,300°,0.25;H_2,300°,1;He,450°, 1;cool in He. Alternatively the catalyst was directly exposed to H_2,100°,2;He, 100°,0.25,cool in He. The system was then evacuated by means of a mercury vapor diffusion pump backed by a liquid-nitrogen trap through F with valves B, C, D, and E closed and A open. Valves A and F were then closed and valve E was opened to admit cyclopentene vapor to the desired pressure which was measured on the Kistler capacitance manometer. Valve A was opened and the catalyst was cooled to −22°C and allowed to stand until the pressure had become constant. During this period, the cyclopentene should have become uniformly distributed throughout the catalyst. The temperature was then lowered to −75° (Dry Ice–ethanol), the system was evacuated, valve A was closed, and valves D and G were opened while evacuation continued. After the valves F and H to vacuum had been closed, valve I was opened to admit hydrogen to the desired pressure, as read on the Kistler. $P(H_2)$ was 100 Torr unless otherwise stated. Valve G was then

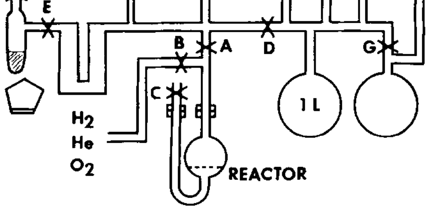

FIG. 1. Apparatus.

closed and valve A opened to start hydrogenation. As hydrogenation proceeded, the pressure drop was measured by the Barocel differential capacitance manometer and recorder. Before valve A was opened, the zero of the Barocel was adjusted to allow approximately for the expansion into the 14.5-cm^3 volume between valves A, B, and C. The amount of cyclopentene adsorbed on the Pt/SiO_2 was calculated from the pressure of cyclopentene and the known volume between valves A, E, D, and F. The volume of the hydrogen ballast bulb was 1 liter and the total volume containing hydrogen during reaction was about 1250 cm^3. Thus, $\Delta P(H_2)$ could be converted to the moles of hydrogen consumed. If a catalyst sample was to be reused, it was exposed again to the pretreatment used in the series.

Most experiments were run at loadings of cyclopentene of one molecule per nm^2 which we shall call *standard coverage*. This corresponds to 440 μmol and 54.3 Torr in the cyclopentene dosing volume of the apparatus. A number of experiments were run at standard coverages of 0.5 and 0.2. Molecular models suggest that one molecule of cyclopentene blocks about 6 atoms of platinum. If so, the amount of cyclopentene adsorbed on the platinum would be 3–24 μmol depending upon the catalyst (see Table 1). Thus 94+% of the cyclopentene in the system was adsorbed on the silica gel at standard coverage by cyclopentene, but a smaller fraction was adsorbed at lower coverages assuming that the platinum was always covered by cyclopentene.

The pressure of cyclopentene adsorbed on 1.0 g of 120–140 mesh Davison Grade 62 silica gel was measured. The silica gel was first treated H_2,300°,1;He,450°,1. In a second run, it was retreated H_2,200°,1 and evacuated for 30 min at 200°C. Cyclopentene at a coverage 0.5 that of the standard coverage was adsorbed on the silica gel as described for adsorption on Pt/SiO_2 catalysts. After 30 min at -75°C the reactor was isolated and the remainder of the system was evacuated. The valve to pumps was then closed and that to the reactor was opened. The pressure rose and became constant after about 1 min. After the first cycle, the pressure rise was the same for subsequent cycles and was 0.006–0.008 Torr.

RESULTS AND DISCUSSION

In the hydrogenations of cyclopentene on Pt/SiO_2 described in this paper, more than 99.99% of the cyclopentene was adsorbed on the catalyst and less than 0.01% of the cyclopentene was in the gas phase. Of the adsorbed cyclopentene greater than 94% was adsorbed on the silica and less than 6% was adsorbed on the platinum.[3] From the data on the hydrogenation of di-t-butyl nitroxide (*2*) described in the Introduction, we believe that hydrogenation of cyclopentene involves transport of the olefin from silica to platinum by either surface migration or vapor phase migration. Consideration of which form of transport is involved will be postponed until later in this paper. Olefin on platinum then undergoes hydrogenation by hydrogen which adsorbs on the platinum from the gas phase.

At *standard coverage* (1 molecule of cyclopentene per nm^2) on Pt/SiO_2 which had received the standard pretreatment, the rate of consumption of hydrogen at -75°C was constant until about 70% of the expected consumption of hydrogen had occurred. Of course the end of the zero order range could not be identified very accurately. The rate then declined until the hydrogenation was about 94% complete, at which time it had become very slow. Typical runs are shown in Fig. 2. In runs with 0.5 of the standard coverage, the zero order section extended only to about 35% of the calculated total consumption and, with a coverage of 0.2, the rate declined from the beginning. In all cases, the rate had become

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[3] Jutand, A., Vivien, D., and Conard, J., [*Surf. Sci.* **32,** 258 (1972)] investigated by NMR the adsorption of butenes on 2 wt% Pt/Al_2O_3 at -70 to 20°C and concluded that a large majority of the butene molecules was adsorbed on the Al_2O_3.

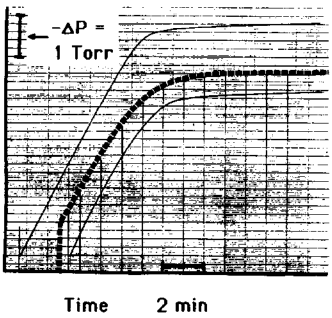

FIG. 2. ΔP in Torr vs time in minutes for hydrogenations on 91.7-Pt/SiO_2. Upper curve for a coverage of about 1 molecule of cyclopentene per nm^2, lower curve for a coverage of about 0.6.

very slow when about 0.06 molecules of cyclopentene per nm^2 remained. If the catalyst was warmed from −75 to 30°C and then returned to −75°C, total consumption of hydrogen corresponded to 100% hydrogenation. Figure 3 represents such an experiment.

Thus, at −75°C, when the standard coverage of cyclopentene exceeded about 0.3, the rate of transport of cyclopentene was large enough to keep the surface of platinum saturated with adsorbed olefin. At smaller coverages, the rate of transport became inadequate to maintain saturation and below a coverage of about 0.06 the rate of transport became very slow.

All values of the turnover frequency per Pt_s (N_t) in this paper were calculated from the zero order sections of recordings of hydrogen consumption vs time. N_t's for catalysts given the standard pretreatment are listed in Table 1.

Catalysts 47.2%-Pt/SiO_2 and 91.7%-Pt/SiO_2 were investigated extensively. Reproducibility between samples of a catalyst and before and after a repretreatment of one sample of catalyst was not very good. This lack of reproducibility probably resulted from varying degrees of formation of slowly reacting species on the surface of the platinum particles when the platinum devoid of H* was exposed to cyclopentene at −22°C. The slowly reacting species may be adsorbed cyclopentadienenyl (*8*). For example, six samples of 91.7%-Pt/SiO_2 were employed. The average value of the turnover frequency taken over all runs was 0.0095 sec^{-1} at standard coverage with the extreme values being 0.0070 and 0.0116 sec^{-1} if one eliminates one high value (0.0131 sec^{-1}) in the 20 runs under consideration. The average N_t for 47.2-Pt/SiO_2 was 0.0075 sec^{-1} (0.0053 to 0.0114 sec^{-1} not counting a few runs in which the catalyst appeared to have become deactivated). Despite the experimental scatter, the data of Table 1 indicate that values of N_t increased somewhat with increasing percentage exposed.

The pretreatment H_2,100° was investigated only with 47.2-Pt/SiO_2. The average value of N_t was 0.00274 sec^{-1} over four runs, a value roughly 40% of that after the standard pretreatment. The extreme variation in the four runs was 8%, considerably less than after the standard pretreatment, probably because the surface of the platinum was covered by H* when the cyclopentene was introduced at −22°C.

In separate experiments on 47.2-IonX pretreated H_2,100°,1, 100 μl of water or of t-butyl alcohol was evaporated onto the catalyst before introduction of cyclopentene to a coverage of 0.5. The rate with water was somewhat higher than in its absence and that with t-butyl alcohol was

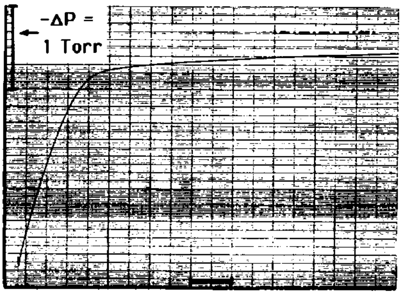

FIG. 3. ΔP in Torr vs time in minutes for hydrogenation on 47.2-Pt/SiO_2 at a coverage of 0.5 molecule of cyclopentane per nm^2. Dashed line at top shows the total ΔP after warming to 31°C and cooling again to −75°C.

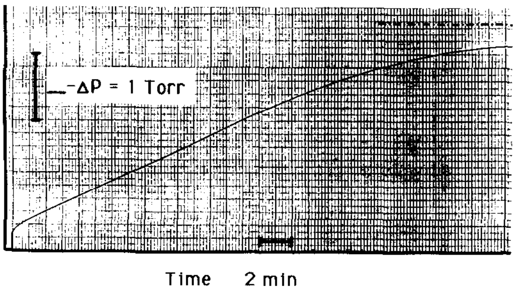

FIG. 4. ΔP in Torr vs time in minutes for hydrogenation on 40-Pt/Al_2O_3 at a coverage of 0.5 molecule of cyclopentene per nm^2. Dashed line at top shows the total ΔP after warming to 31°C and cooling again to −75°C.

somewhat lower, but both were probably within the range of reproducibility. These experiments were run to see whether water or t-butyl alcohol would occupy the sites which strongly adsorbed cyclopentene and, thus, augment the fraction of cyclopentene which reacted in the zero order section. Indeed, the zero order sections extended to nearly twice the fraction hydrogenated normally observed at a coverage of 0.5.

Two runs at a coverage of 0.5 on 40-Pt/Al_2O_3 pretreated H_2, 100° gave almost the same N_t, 0.0018 sec^{-1}. The zero order range was 63%, considerably longer than the 35% observed with Pt/SiO_2. The recording of hydrogen consumption vs time is shown in Fig. 4. The effect of the pressure of hydrogen on rate was investigated on 91.7-IonX after the standard pretreatment by runs at 95, 289, and 682 Torr. Rates were proportional to $P(H_2)^{0.46}$, but given the level of reproducibility one can conclude only that the order in hydrogen was in the vicinity of 0.5. The average value of N_t at $P(H_2) = 682$ Torr was 0.023 sec^{-1}. In previous work with Pt/SiO_2, N_t for the hydrogenation of propylene in a flow reactor at −53°C, P(total) = 1 atm, had been found to be 0.33 sec^{-1} for 81-Pt/SiO_2-IonX (*9*). Extrapolated to −75°C, N_t would be 0.036. The N_t's for the hydrogenations under two quite different conditions are rather close.

Cyclooctene was hydrogenated at −22°C on 47.2-IonX, standard pretreatment, and 0.2–0.3 of the standard coverage. N_t was 0.018 sec^{-1} and the zero order range was about 20%. At −22°C, the saturated vapor pressure of cyclooctene is about 0.4 Torr as judged from that of 1,2-dimethylcyclohexene (*10*) which has nearly the same boiling point as cyclooctene, 138°C.

Mechanism. Hydrogenation of molecules of cyclopentene at platinum particles must be preceded by migration of cyclopentene from silica gel to the platinum. Hydrogenation does not appear to occur by spillover of hydrogen to the silica gel. If it did and if the rate was that of reaction of atoms of hydrogen with adsorbed cyclopentene, one would not expect to find any zero order section of the rate curve, since the areal concentration of cyclopentene steadily decreases with time (*4*). Further, in previous work, the free surface of the support of Pt/SiO_2 and Pt/Al_2O_3 had been converted into a $Si(CH_3)_3$-covered surface by exposure to hexamethyldisilazane. Such conversion had little effect on rates of hydrogenation of ethylene in the gas phase at −46.5°C or of cyclopentene in solution at 20°C (*1*). It is difficult to see how an atom of hydrogen could be bound so strongly to a methyl surface as to compensate for the 435 kJ bond dissociation energy of hydrogen. Good agreement between percentage exposed measured by hydrogen chemisorption at 25°C, transmission electron microscopy, and X-ray diffraction has been found by a number of groups. In particular such agreement was found for some of the catalysts of Table 1 (*6*). Thus, the amount of hydrogen which spills over to the surface of silica gel at 25°C can at most be only a few percent of that which adsorbs on the surface of the platinum of catalysts of low loading by platinum. Further, Schlatter and Boudart (*11*) found that the rate of ethylene hydrogenation at −50°C on Pt/SiO_2 was unaffected by dilution by silica gel or alumina provided diluent and catalyst were free of contamination by organic matter.

The pressure of cyclopentene from silica gel at 0.5 of the standard coverage, 0.5 molecule per nm^2, was about 0.007 Torr at −75°C. This is 0.01 of the saturated vapor pressure of cyclopentene at that temperature (*10*). Assuming that cyclopentene and cyclopentane have the same cross-sectional area in the plane of the molecules, that area is about 0.40 nm^2 (*12*). Thus, standard coverage corresponds to about 0.4 monolayers of cyclopentene. Although there are few reported isotherms on wider pore silica gel, the value 0.01 appears to be reasonable. Thus, at −45°C for 1-butene on a silica gel dehydroxylated at about 500°C, P/P_0 was 0.2 at monolayer coverage ($\theta = 1$) and 0.03 at $\theta = 0.4$ (*13*). Results with butane were similar. Interaction between butane and butene with the silica surface was not strong. The constant c in the BET equation was small, 6.2 for butane and 11.6 for 1-butene. At θ less than unity and at the same pressure, the adsorption of 1-butene was larger than that of butane but only by about 40%. Thus, during hydrogenation of cyclopentene, almost all of the cyclopentane formed would remain adsorbed and would not interfere with the measurement of conversion by measurement of ΔP. In general, in adsorption, $\Delta H_{\text{desorption}}/\Delta H_{\text{evap}}$ is greater than unity, but the ratio is not large for alkenes and alkanes on silica in accord with the small values of c. At a monolayer, in the case of butane just cited, 25 vs 22 kJ mol^{-1}; for benzene, 43.9 vs 36 kJ (*14*); and for cyclohexane, 41.8 vs 35 kJ (*14*). The values of ΔH_{evap} are from Ref. (*10*).

Crystallites of Pt are uniformly distributed throughout the granules of silica gel in catalysts prepared by ion exchange (*15*). The separation between particles of Pt, d in Table 1, was calculated very roughly by assuming that the particles in 1 g were distributed in a (1 × 1) pattern on the 265 m^2 of that 1 g. In the case of 28.1-Pt/SiO$_2$, the average distance between particles of platinum is 44 nm. Let us assume that each platinum crystallite leads to the hydrogenation of the molecules of cyclopentene adsorbed on the walls of a cylindrical tube 14 nm in diameter and 44 nm long as shown in Fig. 5.

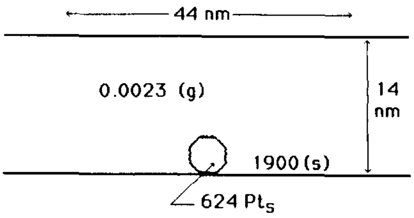

FIG. 5. Schematic representation of a section of 28.1-Pt/SiO$_2$.

This represents a crude approximation to the texture of silica gel, but it should be adequate for present purposes. The average number of molecules of cyclopentene in the gas phase in the tube is 0.0023 at 0.007 Torr. The number of adsorbed molecules (on Pt and silica) is 1900 and the average number of atoms of Pt$_s$ is ~624. With N_t = 0.0025 sec^{-1}, each crystallite of platinum leads to the hydrogenation of 1.6 molecules of cyclopentene per second. Despite the low pressure of cyclopentene, transport through the vapor phase is not immediately excludable, since, in general, with a sticking coefficient of unity, a monolayer is formed on a clean surface in 1 sec at P = 10^{-6} Torr.

Presumably, migration of cyclopentene occurs both by gas phase and surface migration; the question is which dominates? Are we dealing with an unprecedented case of a vapor phase hydrogenation in which the pressure of cyclopentene is only 0.007 Torr and in which the very severe diffusional problems which would be present in a conventional reactor are avoided by "delivering" the cyclopentene uniformly throughout the catalyst granules? Or are we dealing with an unusual reactor in which cyclopentene in a fluid phase plays a negligible role? Either case could lead to the observed kinetics of hydrogenation: a segment zero order in cyclopentene, followed by a segment of lower rate and finally a segment of very low rate. Because of the nonuniformity of the surface of silica gel, as θ is reduced below unity, $-\Delta H_{\text{ads}}$ becomes steadily larger. At smaller times on stream, the rate of supply of cyclopentene to the particles of platinum might be large enough to keep the platinum surface covered either by vapor phase or by surface migration. At larger times, migration both via the vapor phase and by the surface would decrease in rate as θ decreased.

In the previous hydrogenation of di-t-butyl nitroxide on Pt/SiO$_2$ and Pt/Al$_2$O$_3$ (*2*), surface migration must have been heavily predominant. One can roughly estimate the vapor pressure of the nitroxide at -75°C by calculating the vapor pressure of 2,2,3,4,4-pentamethylpentane (*10*). This pressure is about 0.0004 Torr. Thus, at a fractional monolayer coverage, the pressure of nitroxide in equilibrium with adsorbed nitroxide is about 0.000004 Torr, or less if one considers that nitroxide is hydrogen-bonded to surface OH groups (*2*).

The activation energy for migration via the vapor phase should be equal to ΔH_{des}. That for surface migration should be a fraction of ΔH_{des}, since, at the top of the barrier between adjacent sites for adsorption, considerable adsorption energy would still remain. Thus, higher temperatures would tend to favor the predominance of vapor phase migration and lower temperatures, of surface migration. There is a rather large body of information dealing with surface migration on metals (*16*), but much less dealing with migration on silica and alumina. Fortunately, however, there appears to be enough for present purposes. The techniques of interest here for assessing the nature of migration in porous bodies are measurement of the rate of permeation through a plug of porous material and pulsed NMR. In the first case, the rate of permeation of a vapor through a porous plug is measured at a temperature at which considerable adsorption occurs. This is corrected for Knudsen diffusion though the gas phase by the rate of permeation of a gas, usually helium or nitrogen, which is not adsorbed at that temperature. Thus, one can determine the ratio of surface to gas phase migration. The rate of propylene permeation through Vycor (a material whose surface resembles that of silica gel) with 2.8-nm pores has been examined at about 0°C (*17*). Rates of permeation by nitrogen and helium were also measured. It was concluded that permeation of propylene through Vycor went 20% through the vapor phase and 80% by surface migration. One would conclude that cyclopentene at -75°C would involve a higher proportion of surface migration than propylene at 0°C.

The diffusion of benzene and of cyclohexane on a silica gel with an average pore diameter of 6 nm and no micropores has been studied by pulsed NMR techniques (*14*). Above about 10°C, the activation energy for diffusion was about ΔH_{des}. Below 0°C, the activation energy was much smaller, 1.1–1.4 kcal mol^{-1}. Thus, above 10°C, transport was primarily by Knudsen diffusion in the vapor phase, below 0°C, by surface migration. We conclude, therefore, that surface migration of cyclopentene heavily dominated during the hydrogenation of cyclopentene at -75°C.

Coupling reactions of several free radicals prepared on silica gel by photolysis have been investigated. They provide information on surface mobility, although the possibility of migration via the vapor phase was not considered in these papers. $\text{Ph(CH}_3)_2\text{C—N=N—C(CH}_3)_2\text{Ph}$ has been photolyzed on silica gel at -196°C to produce the cumyl free radical, $\text{Ph(CH}_3)_2\text{C}\cdot$ (*18*). At -129°C, the free radical becomes translationally mobile and its EPR signal decays with the formation of dicumyl with a half-life of 1 h. At this temperature, the migration of the free radicals occurs almost certainly by surface migration. A similar experiment has involved (4-methoxybenzyl)C(O)O-(4-methylbenzyl) in which CO$_2$ is eliminated to form free radicals (*19*). The radicals are mobile at $T > -50$°C. If the cumyl free radical has about the same vapor pressure as cumene, its vapor pressure at -50°C would be about 0.02 Torr (*10*). Migration must almost surely have proceeded by surface diffusion at this temperature. Photolysis of a mixture of diazoisobutyronitrile, $(CH_3)_2(CN)C{-}N{=}N{-}C(CN)(CH_3)_2$, and diazoisobutyronitrile-d_{12} at 25°C led to the formation of some d_6 products (*20*). That migration proceeded predominantly by the surface and not by the vapor phase is less clear in this case.

One must consider, however, the experiment of Adamson and Slawson (*21*). In this, two layers of silica gel were separated by a Teflon spacer with a circular hole. One layer of silica gel contained ^{14}C-labeled palmitic acid. Transport of palmitic acid was observed to occur to the other layer of silica gel. At 85°C, a typical temperature of an experiment, the vapor pressure of palmitic acid is 0.002 Torr. Transport between the layers of silica gel must have proceeded by vapor phase transport, but most of the palmitic acid transported came from the pores of the silica gel. One would expect that the activation energy for the overall process to be equal to ΔH_{des}, but it was distinctly less than that. The authors proposed that "if molecules in the middle region of a pore still experience some adsorption potential, then, in effect, they are only partially desorbed." However, removal of a molecule from a pore to the outside surface would require an additional energy which would bring the measured E_a up to ΔH_{des}. Thus, it does not seem to have been unequivocally established that migration within the pores occurred by Knudsen diffusion.

Overall, the results of Refs. (*14, 17–19*) would appear strongly to indicate that the hydrogenation of cyclopentene at −75°C involved primarily surface migration. At coverages of cyclopentene greater than 0.3 molecules per nm^2, the rate of surface migration of cyclopentene was adequate to maintain saturation of the platinum surface with cyclopentene. At lower coverages this was no longer true and the rate of hydrogenation decreased probably as a result both of the reduced areal concentration of cyclopentene and of the slower migration of the more strongly bound cyclopentene that increasingly dominates at low coverages because of nonuniformity of the surface of silica gel. Owing to the latter effect the rate of hydrogenation became very slow below a coverage of 0.06 molecules of cyclopentene per nm^2. In the hydrogenation of di-t-butyl nitroxide at −70°C, there was no zero order section and the rate was approximately first order in nitroxide over a substantial initial region. Presumably, the rate of migration of nitroxide was slower than that of cyclopentene, probably because the nitroxide was more strongly adsorbed because of hydrogen-bonding to surface silanol groups.

Cyclooctene was chosen as an additional olefin to examine. It has a structure similar to cyclopentene, it competes with almost the same effectiveness as cyclopentene in competitive hydrogenations with other olefins, but at 25°C its rate of hydrogenation is only 0.08 that of cyclopentene (*22*). At −22°C, N_t was 0.018 sec^{-1}. Overall, the behaviors of cyclopentene and cyclooctene were similar and, judging from Ref. (*14*), surface migration must have heavily predominated during the hydrogenation of cyclooctene.

In cryoenzymology (*23*) enzyme reactions have been studied at low temperatures in solvent systems which remain liquid. In some cases, one or more steps in the catalytic cycle become so slow that further reaction of an intermediate is blocked and the overall reaction becomes that of formation of the intermediate with catalysis being blocked. Such effects have been noted in heterogeneous catalysis at higher temperatures. For example, in the decomposition of formic acid, formation of surface formate may occur at a lower temperature, whereas decomposition occurs only at a higher temperature. In the hydrogenation of cyclopentene at −75°C, one could imagine that the reaction would stop at monoadsorbed cyclopentane, $^*C_5H_9$. This, however, does not occur. For example, in hydrogenation at a coverage of 0.2 on 47.2-Pt/SiO$_2$, ~23% of the cyclopentene should be adsorbed on the surface of the platinum particles. No break in the hydrogenation plot is observed at consumptions of hydrogen corresponding either to the formation of $*C_5H_9$ or C_5H_{10} from the cyclopentene initially adsorbed on the surface of Pt.

We are not sure as to why the observed order in hydrogen during hydrogenation is about 0.5 rather than unity as is normal. If, as we think (*24*), the rate of hydrogenation on platinum catalysts is that of the adsorption of hydrogen, then the usual order in hydrogenation of unity requires that H_2 once adsorbed reacts very rapidly so that coverage by *H at sites accessible to hydrogen is kept very low. Perhaps at −75°C, the relative rate of reaction of H* is less and coverage by hydrogen becomes larger. In such a case, the kinetic order in hydrogen would become less than unity.

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